

## **PROCESS FOR DESULFURIZATION WITHOUT CONSUMPTION OF HYDROGEN**

This invention relates to a process for desulfurization of hydrocarbon-containing fractions that contain sulfur with contents that are at least greater than 5 ppm and that can go up to 5% by weight. This process finds its application in particular in the treatment of petroleum fractions whose boiling points are typically higher than 150°C and even 200°C. In particular, this process advantageously makes it possible to desulfurize a kerosene or a gas oil that is obtained from the distillation of crude oil or in general any product that is obtained partly or completely from a process for converting a petroleum residue.

Because of environmental requirements, official provisions in the industrialized countries limit the sulfur content in fuels, and more particularly the fuels such as the gas oils, in an increasingly restrictive way. The European specifications impose, for example, a sulfur content in the gas oils that is less than 50 ppm (portion per million) at present, while this limitation should certainly reach 10 ppm in the near future.

To reach this objective, a process for hydrodesulfurization by hydrogenation is routinely used by the refiner so as to eliminate the sulfur that is contained in the hydrocarbon-containing fraction that is to be treated. The sulfur that is present is finally extracted from said fraction in the form of gaseous sulfur or hydrogen sulfide. These processes generally consist in hydrogenating the feedstock in the presence of pressurized hydrogen (2 to 10 MPa) and at temperatures of generally between 300 to 400°C, in the presence of a catalyst with a sulfide base of cobalt and molybdenum or nickel and molybdenum.

The main problem that is linked to this type of process is the high consumption of hydrogen thereof. This hydrogen is generally of a limited quantity on the site of the refinery since it is generally produced in the great majority only during a catalytic reforming stage. Finally, since the specifications that relate to the sulfur contents of the products that are obtained from the refinery are set to become increasingly strict, it can be anticipated that the production of hydrogen by the simple process of catalytic reforming will prove to be, within the refinery, inadequate to meet the demand.

Patent US 3,551,328 describes an alternative process for desulfurization of a heavy hydrocarbon fraction that does not consume hydrogen, in which the sulfur-containing compounds that are contained in said fraction are oxidized in the presence of an oxidizing agent. This oxidation can be done in the presence of a catalyst that comprises an organometallic complex of a metal of groups IV-B, V-B and VI-B of the periodic table. The

thermal instability of such catalysts makes it necessary, however, to carry out the oxidation at a relatively low temperature, which produces relatively long reaction times that are not very compatible with the economic requirements of an industrial-scale operation.

The process that is the object of this invention proposes an alternative solution to hydrotreatment processes. This process comprises selectively oxidizing the sulfur-containing compounds that are contained in a fraction or petroleum fraction into sulfones and sulfoxides.

Upon further study of the specification and appended claims, further objects and advantages of this invention will become apparent to those skilled in the art.

This process uses a more stable catalyst and also makes it possible to have oxidation periods that are short and compatible with an industrial use.

In its more general form, the invention relates to a process for desulfurization of a hydrocarbon-containing fraction that comprises at least one stage of treatment of said fraction with an oxidizing agent in the presence of a catalyst of said oxidation, in which said catalyst comprises at least one metallic oxide of chemical formula  $M_xO_y$ , whereby M is an element that is selected from the group that consists of the elements of groups IV-B, V-B or VI-B of the periodic table.

The catalyst is preferably in bulk form and more preferably essentially consists of the active phase  $M_xO_y$ , i.e., it is constituted at at least 70% by weight, preferably at at least 80% by weight, more preferably at at least 90% by weight, and even at at least 98% by weight, by a metallic oxide of chemical formula  $M_xO_y$  wherein x and y are dependent on the valence of M.

The use of such a catalyst thus makes it possible to reduce the time in which the different reaction phases are brought into contact thanks to a temperature that according to the invention can be between ambient temperature (about 20°C) and 200°C, and even 300°C. The temperature is more preferably greater than or equal to 100°C.

The hydrocarbon-containing fraction that is treated in the process according to the invention can be obtained from the distillation of crude oil or an effluent from the entire cracking unit that is known to one skilled in the art. It is generally called an atmospheric distillate and comprises the kerosene and/or gas oil fraction. Said hydrocarbon-containing fraction is preferably a petroleum fraction whose boiling points are between 150 and 500°C. More preferably, said hydrocarbon-containing fraction comprises a fraction by weight of sulfur-containing compounds of between 5 ppm and 5%.

In the process of desulfurization according to the invention, the temperature of the oxidation reaction is preferably between 40°C and 300°C and more preferably greater than or equal to 100°C.

The pressure of this stage is preferably between 0.1 MPa and 5 MPa, more preferably between 0.1 MPa and 2 MPa, with or without oxygen.

In the catalyst according to the invention, element M is preferably selected from the group that consists of vanadium, chromium, zirconium, molybdenum, tungsten, and titanium, by themselves or in combination. Very preferably, said catalyst comprises a molybdenum oxide. Said catalyst is preferably used in the form of powder, balls or extrudates.

In the process for desulfurization according to the invention, the oxidizing agent is preferably selected from the group that consists of peroxides, hydroperoxides, organic peracids, ozone, oxygen, nitrogen oxides and metallic oxidizing agents, by themselves or in combination.

The process for desulfurization of a hydrocarbon fraction according to the invention preferably comprises at least the following stages:

- a) An oxidation of at least a portion of the sulfur-containing compounds that are contained in said hydrocarbon-containing fraction in the presence of at least one oxidizing agent and a catalyst according to any of the generically or specifically described oxidation steps of the invention, and
- b) A separation of the oxidized sulfur-containing compounds of the products obtained from stage a) by extraction, distillation or adsorption.

Stage b) is preferably an adsorption that is carried out in at least one adsorbent column, whereby said adsorbent is selected from among amorphous oxides such as amorphous aluminas, amorphous silicas or amorphous silica-aluminas or from among the crystallized oxides such as zeolites, clays, or a mixture of at least two of these elements. More preferably, an adsorbent that can be regenerated directly by calcination will be selected.

The desulfurization process according to the invention optionally can also comprise a stage for separation of the catalyst between oxidation stage a) and separation stage b).

#### Brief Description of the Drawing

The invention will be better understood by reading the following description of a non-limiting embodiment of said invention, schematically illustrated by the attached Figure.

The feedstock, for example a hydrocarbon fraction that is obtained from the atmospheric distillation of a crude oil whose boiling point is higher than 150°C and that contains a sulfur fraction, is injected via line 1 into an oxidation unit A. This unit consists of one or more reactors that operate continuously or intermittently, i.e. batch-wise. Most often, a system for mechanical stirring of phases present among reactors and/or a system for recirculation (internal or external) of the batch and/or reagents are provided so as to have the best contact possible between the feedstock, the reagents and the catalyst.

An oxidizing agent is routed via line 2 to oxidation unit A. An oxidation catalyst is either initially present in the unit or injected at the same time as the oxidizing agent via line 2. This oxidizing agent/catalyst pair is able to oxidize selectively the sulfur-containing compounds that are contained in the hydrocarbon fraction. By way of example, the dibenzothiophenes are oxidized into sulfones according to the following reaction:

[Key: Oxidant/Catalyseur = Oxidizing agent/catalyst]

The oxidizing agent that is used is advantageously selected from the class of hydroperoxides and preferably from the group that consists of hydrogen peroxide, tert-butyl hydroperoxide, and cumene hydroxide.

The catalyst comprises at least one oxide of general formula  $M_xO_y$  as defined above, and element M is preferably selected from the group that consists of titanium, zirconium, vanadium, chromium, molybdenum and tungsten. The very preferred metallic oxides are molybdenum oxide  $MoO_3$ , vanadium oxide  $V_2O_5$  or zirconium oxide  $ZrO_2$ , taken either separately or in a mixture.

The catalyst is most often used in the form of balls, extrudates or powder, although any known form of the catalyst can be considered within the scope of this application.

The molar ratios between the catalyst and the sulfur that are contained in the feedstock are most often between 0.0001 and 2000, preferably between 0.001 and 100. These ratios are adjusted by one skilled in the art based on the flow rate of the feedstock and the average temperature of unit B.

The products of the oxidation reaction are routed via line 3 to a unit for separation of catalyst B. This operation is optional and is justified only to the extent that the catalyst that is used is in powdered form and routed with the oxidizing agent via line 2. In the case of a catalyst, in the form of balls or extrudates, already being present in unit A, for example in the form of a fixed particle bed, this operation is generally not useful.

The products of the reaction are then sent into a water elimination unit C via a line 4. Unit C can be a decanter, a coalescer or any other known means that can promote an elimination of the water that is contained in said products of the reaction. This operation is optional, but preferred, because on the one hand, the oxidation of the sulfur-containing compounds is generally not done in an aqueous medium, and the other hand, said oxidation can result in a formation of water in a small quantity that can adversely affect the adsorbent during the following adsorption phase. The water is evacuated via line 5.

The products that are obtained from unit C are then sent via line 6 into a unit D for separation of sulfones and sulfoxides from the hydrocarbon-containing medium. Although the use of a distillation or solvent extraction solvent or any other known means of separation is possible within the scope of this invention, preferably an adsorption unit will be used. For example, columns that are filled with an adsorbent will be used. The adsorbent then advantageously comprises at least one amorphous oxide such as alumina, silica or silica-alumina or a mixture of the latter or a crystallized oxide such as a zeolite or a clay. It will also be possible to employ a mixture of these compounds in adequate proportions within the columns.

After adsorption of sulfones, the effluent, which is low in sulfur-containing compounds, is finally recovered at the outlet of the unit via line 7.

The following examples illustrate in a non-limiting manner some of the advantages of this invention:

**Example 1:** According to the Invention

This example demonstrates the effectiveness of this process for eliminating sulfur-containing compounds contained in a hydrocarbon-containing feedstock.

The feedstock is a gas oil that is obtained from a crude oil whose distillation interval is between 150 and 350°C. This gas oil contains 2% by weight of sulfur.

The oxidizing agent/catalyst mixture is a mixture that consists of tert-butyl hydroperoxide (38 g/liter of feedstock) and bulk molybdenum oxide  $\text{MoO}_3$  (3.2 g/liter of feedstock). This mixture is heated to 100°C. The outlet effluent no longer contains

benzothiophene and dibenzothiophene but corresponding sulfones and sulfoxides. This transformation was demonstrated by gas chromatography.

The mixture that is obtained is then sent to a column that contains an amorphous silica, previously activated under nitrogen at 120°C. This mixture is sent with an adjusted flow rate such that the ratio of the flow rate of feedstock to the volume of catalyst is equal to 1 liter of feedstock per liter of silica and per hour. At the outlet of the unit, the sulfur content of the unit, determined according to known techniques by combustion and chemiluminescence, is equal to 5 ppm.

Several characteristics of the feedstock and the effluents that are obtained from this process are reported in Table 1:

	Feedstock	Effluents
Density	0.82	0.819
Sulfur (% by weight)	2	0.0005

**Table 1**

This comparison shows that the process of the invention makes it possible to obtain products that have a very low sulfur content, according to specifications without the consumption of hydrogen.

Example 4 demonstrates that the presence of a catalyst according to the invention advantageously promotes the oxidation stage of the sulfur-containing compounds compared to comparative examples 2 and 3.

**Example 2:** Oxidation without a Catalyst (For Comparison)

Two grams of oxidized water are dissolved in 20 g of heptane. This mixture is placed in a flask on top of which is a rising condenser. 3.6 g of acetic acid dissolved in 20 g of heptane is added drop by drop into the flask to prepare the peracid. Then, once the peracid is prepared, the feedstock that consists of decane (107 g) that contains about 10% by weight of benzothiophene (1.4 g) is added drop by drop to the peracid. Stirring of the mixture is maintained, then it is heated first to 50°C at atmospheric pressure for 4 hours, then to 100°C at atmospheric pressure for 30 hours. Chromatographic analysis at a regular time interval showed that the benzothiophene is not oxidized in a period of at least 30 hours.

**Example 3:** Oxidation with an Acid Catalyst (For Comparison)

The procedure that is used in this example is the same as in the preceding example. 2 g of catalyst was added to the peracid mixture before the feedstock was introduced, however. In this example, the catalyst used is a sulfonic resin marketed by Rohm and Haas under the trade name Amberlyst 15. The mixture was heated to 50°C at atmospheric pressure for 7 hours, then to 100°C at atmospheric pressure for 15 hours. Chromatographic analyses showed that benzothiophene does not oxidize even after 7 hours of heating.

**Example 4:** Oxidation with a Catalyst According to the Invention

0.28 g of molybdenum oxide is added to a peracid mixture that is identical to that of Example 3. The mixture is heated to 100°C at atmospheric pressure while being stirred for one hour. It appears that at the end of one hour, all of the benzothiophene present in the feedstock has disappeared.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

The entire disclosures of all applications, patents and publications, cited herein and of corresponding French application No. 02/11.472, filed September 16, 2002 are incorporated by reference herein.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.